# Photorefractive properties of Ce- and Ca-doped $Sr_{0.6}Ba_{0.4}Nb_2O_6$

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We present the results of experimental study of the absorption coefficient, two-beam photorefractive coupling constant, and photorefractive response time of a doubly Ce- and Ca-doped $Sr_{0.6}Ba_{0.4}Nb_2O_6$. This crystal displays enhanced photorefractive response at near infrared wavelengths when compared to Ce-doped SBN:60. The temperature dependence of the coupling constant over the range from $-30$ to 40 °C has also been studied.

Photorefractive undoped, cerium-doped, and iron-doped strontium barium niobate (SBN) has been successfully grown and shown to satisfy the important requirements for optical processing applications of low response time, high photorefractive coupling constant, and high optical quality.[1] Furthermore, SBN has been shown to have important advantages over $BaTiO_3$ in the areas of controllability of the photorefractive properties, physical ruggedness, resistance to temperature changes and applied electric fields, and size. In this letter, we report on the photorefractive properties of a doubly cerium- and calcium-doped SBN:60 crystal, which has shown enhanced response at near infrared wavelengths over previously studied cerium-doped SBN:60.

Strontium barium niobate belongs to a class of tungsten bronze ferroelectrics that are pulled from a solid solution of alkaline earth niobates. SBN in general has a formula of $Sr_xBa_{1-x}Nb_2O_6$, so SBN:60 represents $Sr_{0.60}Ba_{0.40}Nb_2O_6$. Undoped SBN is transparent and can be grown with a wide range of ferroelectric and electro-optic properties by changing the cation ratio. The SBN unit cell contains ten $NbO_6$ octahedra, with only five alkaline earth cations to fill ten interstitial sites.[2] Therefore, the incompletely filled structure permits the addition of a wide range of dopants in the SBN crystal.

The point group symmetry of SBN is $4mm$, which implies that its electro-optic tensor is nonzero. The dominant electro-optic coefficient is $r_{33}$, which has been determined to be 420 pm/V for SBN:60.[3] In order to obtain the large values of the electro-optic coefficient in SBN, the crystal must be poled by heating above its Curie temperature and cooling back to room temperature with an applied electric field of 5–8 kV/cm. In SBN:60, this ferroelectric to cubic phase transition is at approximately 75 °C.[3]

The double-doped SBN:60 single crystal was grown at Rockwell International Corporation using the Czochralski technique. The resulting sample was an optical quality, $5\times6\times6$ mm cube. Cerium doping has been shown to result in increased absorption over the visible region over undoped SBN.[1] Introduction of calcium as a second dopant in the double-doped SBN:60 with the cerium in the nine-fold coordinate sites results in an additional absorption band in the red, centered around 650 nm, as shown in Fig. 1. Therefore, we expect the crystal to have enhanced response at longer wavelengths over the single-doped SBN:60:Ce due to the increased photoexcitation of carriers at these wavelengths.

The photorefractive properties of the SBN:60:Ce,Ca sample were studied using the two-wave mixing experiment.[1] By measuring $I_1(0)$ and $I_2(0)$, the incident intensities of the two beams, and $I_1(l)$ and $I_2(l)$, the intensities after passing through the crystal, the two-beam coupling constant $\Gamma$ can be obtained through the equation

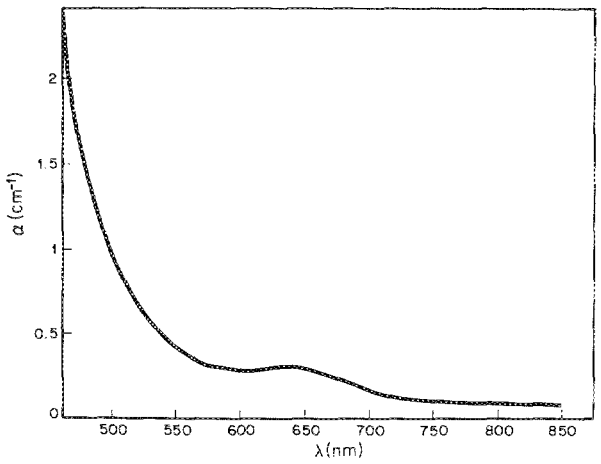


FIG. 1. Absorption spectrum of lightly cerium- and calcium-doped SBN:60:Ce,Ca.

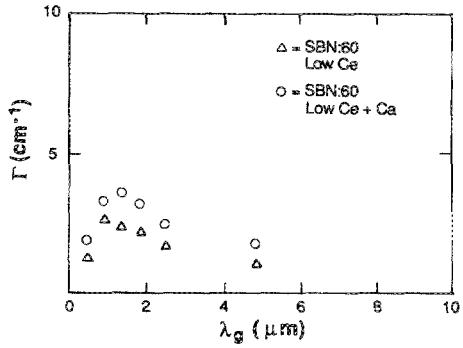


FIG. 2. Two-beam coupling constant $\Gamma$ as a function of grating wavelength $\lambda_g$ in SBN:60:Ce,Ca for $I_0 = 1$ W/cm$^2$.

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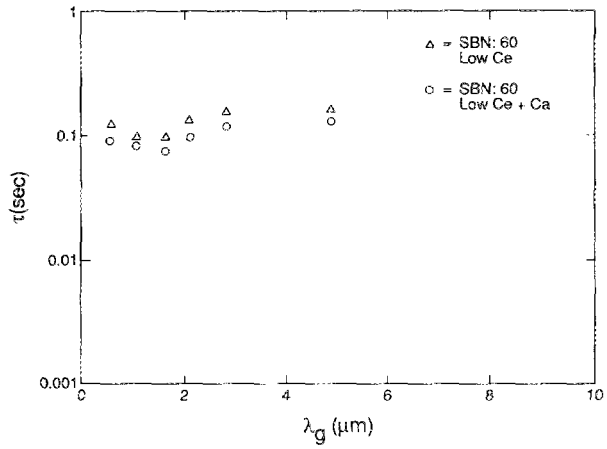


FIG. 3. Photorefractive response time $\tau$ as a function of grating wavelength $\lambda_g$ for $I_0 = 1$ W/cm$^2$.

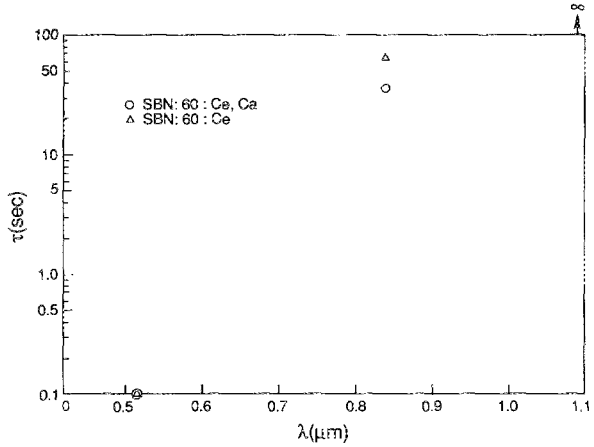


FIG. 5. Photorefractive response time $\tau$ at 514.5, 840, and 1090 nm for SBN:60:Ce and SBN:60:Ce,Ca at $\lambda_g = 2\ \mu$m.

$$\Gamma = \frac{1}{l}\ln\left(\frac{I_2(l)I_1(0)}{I_1(l)I_2(0)}\right). \tag{1}$$

The time dependence of the two-beam coupling constant $\Gamma(t)$ was used to obtain the characteristic rise time $\tau$ of the material.

The experimental values for the coupling constant $\Gamma$ and the response time $\tau$ of the SBN:60:Ce,Ca crystal for various grating wavelengths at room temperature are shown in Figs. 2 and 3. With incident beam intensities of $\sim 1$ W/cm$^2$ and $\lambda_g = \lambda_{g,max} \sim 1.4\ \mu$m, the coupling constant $\Gamma$ was 3.5 cm$^{-1}$ and $\tau$ was 0.1 s. Comparison with the data previously obtained for low Ce-doped SBN:60 indicates that the values for $\Gamma$ and $\tau$ are comparable for the two crystals.

The wavelength dependence on the steady-state photorefractive coupling constant and response time is shown in Figs. 4 and 5 for 514.5 nm, 840 nm, and 1.09 $\mu$m at a grating wavelength of 2 $\mu$m. As expected, the SBN:60:Ce,Ca exhibits a stronger response at 840 nm than SBN:60:Ce, with $\Gamma = 1.5$ cm$^{-1}$ and $\tau < 35$ s for SBN:60:Ce,Ca vs $\Gamma = 0.29$ cm$^{-1}$ and $\tau > 60$ s for SBN:60,Ce. At 1.09 $\mu$m, neither crystal was photorefractive. Again, we attribute this enhanced near infrared response of SBN:60:Ce,Ca to the additional absorption band centered at 650 nm contributing additional donors photoionizable by the lower energy incident light. However, considering that both tungsten bronze materials cut off between 840 nm and 1.09 $\mu$m while $BaTiO_3$ still exhibits a significant response at 1.09 $\mu$m, this implies that the energy levels created by cerium and calcium impurities in SBN must necessarily lie deeper in the band gap than those formed by iron in $BaTiO_3$.

There is a built-in temperature dependence on the steady-state $\Gamma$ through the characteristic fields in the expressions derived from the band transport model.[4-6] For the stationary grating, one-carrier, one species case, the coupling constant is given by

$$\Gamma \propto \frac{E_q E_d r}{E_d + E_q}, \tag{2}$$

where $E_d = 2\pi k_B T/\lambda_g e$ and $E_q \propto \lambda_g/2\pi\epsilon$.

The experimental data for the coupling constant of the SBN:60:Ce,Ca as temperature was varied from $-30$ °C to 40 °C are shown in Fig. 6 and show $\Gamma$ increasing as the crystal was cooled. The dielectric constant was determined by measuring the low-frequency impedance of the crystal as a function of temperature. As expected, the dielectric constant, and therefore the electro-optic coefficient $r$, was found to be decreasing as the temperature decreased, which was

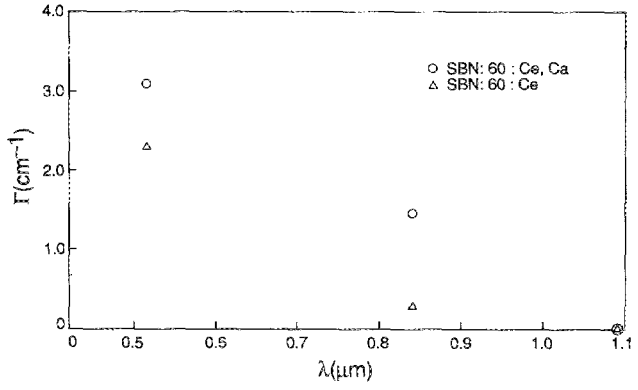


FIG. 4. Two-beam coupling constant $\Gamma$ at 514.5, 840, and 1090 nm for SBN:60:Ce and SBN:60:Ce,Ca at $\lambda_g = 2\ \mu$m.

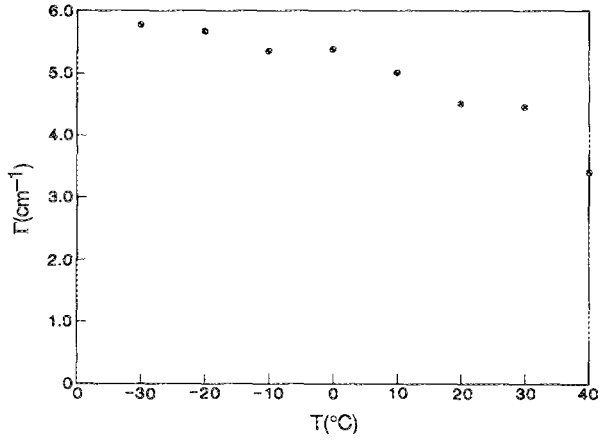


FIG. 6. Two-beam coupling constant $\Gamma$ of SBN:60:Ce,Ca as a function of temperature. $I_0 = 0.14$ W/cm$^2$.

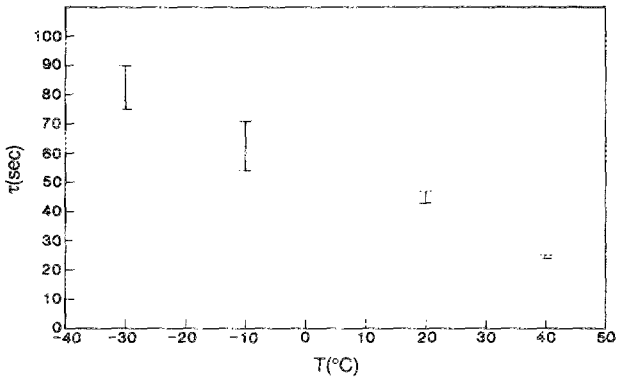


FIG. 7. Dark decay time of SBN:60:Ce,Ca. For the purposes of this letter, the dark decay time was defined to be the time required for the diffraction efficiency of the crystal, having been exposed with two beams with modulation depth 1.00 and intensity 0.14 W/cm$^2$ and read with a probe beam of $<90\,\mu$W/cm$^2$, to decay to $e^{-1}\eta_0$.

expected since we are moving away from the phase transition temperature at around 75 °C. This would imply that $\Gamma$ increases with temperature because of the dependence of $\Gamma$ on $\epsilon$. However, the current band transport model does not account for the dark conductivity of the crystal, assuming that once a space-charge field is formed, the field remains in place indefinitely unless deliberately erased. This dark conductivity effect may be responsible for the inverse temperature dependence of $\Gamma$ that we observed in this particular crystal. If this dark conductivity factor were to be present, the coupling constant will decrease as the charge carriers forming the periodic space-charge field leaked through the bulk material and reduced the efficiency of the photorefractive grating. Figure 7 shows that the dark conductivity, measured through the dark decay time of the crystal, does indeed increase with temperature, resulting in the lower coupling at higher temperatures.

In summary, we have succeeded in growing optical quality double-doped SBN:60:Ce,Ca and showed it to be photorefractive. Its steady-state two-beam coupling constant of $\sim$2.5 cm$^{-1}$ and response time of 0.1 s at a beam intensity of 1 W/cm$^2$ were comparable to the values obtained previously for single-doped SBN:60:Ce. Moreover, we have shown that SBN:60:Ce,Ca has improved response over SBN:60:Ce at 840 nm. The temperature dependence of the photorefractive coupling, electro-optic coefficient, and dark conductivity was also investigated and showed the coupling constant increasing when the crystal was cooled, which can be attributed to its decreased dark conductivity at lower temperatures.

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